

Surface Stability of Semifluorinated Mechanically Assembled Monolayers (MAMs)

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Introduction: It has now been well established that the surface properties of materials can be successfully tailored by depositing self-assembled monolayers (SAMs) made of ω -functionalized alkanes. It has been recognized that the wetting properties of SAMs and their stability are governed by the intimate interplay between the chemical nature of the terminus of the monolayer molecule (ω -) and the packing within the SAM. While the ω -character is fixed by the chemical structure of the terminal group, the packing can be altered by varying the density of the grafting points at the surface. However, tailoring the grafting density of the SAM chains is not an easy task. The SAMs are usually formed via self-assembly processes that are governed by the chemical and structural nature of the SAM molecules and the means of their attachment to the solid surface. However, when combined with mechanical manipulation originating from the substrate, the grafting density and thus the chain packing can be successfully tailored.

Methods and Materials: Recently we have demonstrated the feasibility of mechanically assisted assembly by fabricating high-density semifluorinated (SF) organosilane-based monolayers on polydimethylsiloxane (PDMS) network films [1]. In this technique, a pristine PDMS network film is mechanically stretched by a certain amount, Δx , and then exposed to UV/ozone (UVO) treatment to produce the surface $\equiv\text{Si}-\text{OH}$ groups. The SF-chlorosilane molecules are deposited from the vapor phase and form an organized SAM. Finally, the strain is released from the modified PDMS substrate, which returns to its original size, causing the grafted molecules to form a densely organized MAM ("mechanically assembled monolayer"). To validate the close packing and the resulting low mobility of the SF molecules on the surfaces of the SF-MAMs, experiments using near-edge X-ray absorption fine structure (NEXAFS) were carried out on MAMs prepared from $\text{F}(\text{CF}_2)_8(\text{CH}_2)_2\text{SiCl}_3$ (F8H2-MAM) with $\Delta x = 0\%$ and $\Delta x = 70\%$ that were exposed to water for the same time intervals. By monitoring the partial electron yield (PEY) NEXAFS, the orientation of the SF chains on the SF-MAM surfaces can be determined.

Results: Figure 1 shows the values of the average tilt angles of the fluorocarbon helix, $\langle\tau_{\text{F-helix}}\rangle$, that were determined from PEY NEXAFS spectra collected from F8H2-MAMs with $\Delta x = 0\%$ (squares) and $\Delta x = 70\%$ (circles). The F8H2-MAMs prepared on unstretched PDMS-UVO substrates ($\Delta x = 0\%$) stand almost perpendicular to the sample surface. However, the data in Fig. 1 shows that when exposed to water, the chain orientation starts to disappear very rapidly and after about 1 day of water exposure, the F8H2-MAMs with $\Delta x = 0\%$ disorient completely. The behavior of the F8H2-MAMs prepared on PDMS-UVO substrates with $\Delta x = 70\%$ is very different. Specifically, the NEXAFS data reveal that $\langle\tau_{\text{F-helix}}\rangle$ on samples exposed to water for up to 7 days is indistinguishable from that measured on the same specimen before the water exposure! These results thus provide further evidence that the F8H2 molecules in MAMs with $\Delta x = 70\%$ are closely packed and mechanically interlocked; this interlocking hinders the chain's tendency to move and reconstruct on the MAM surface. These results thus show that the SF-MAM surfaces possess superhydrophobic properties and that these surfaces are resistant to surface reconstruction. We attribute this unusual behavior to the extremely high packing densities of the MAMs – values that can only be achieved using this novel assembling method.

Conclusions: We have shown that these MAMs exhibit superhydrophobic properties that do not deteriorate even after prolonged exposure to polar liquids (such as water), conditions under which most conventionally prepared SF materials fail to keep their good barrier properties. NEXAFS experiments demonstrated that these long-lasting superhydrophobic properties of the SF-MAMs are a consequence of close packing and mechanical interlocking of the SF moieties on the PDMS substrates.

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References: [1] Genzer, J. and Efimenko, K., submitted for publication.

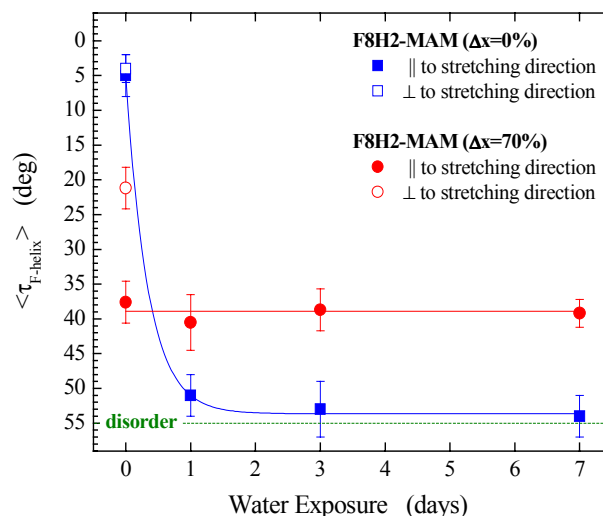


Figure 1. The dependence of the average tilt angle of the fluorinated helix, $\langle\tau_{\text{F-helix}}\rangle$, in F8H2-MAMs on the exposure time of the F8H2-MAM to water. The squares and circles denote $\langle\tau_{\text{F-helix}}\rangle$ in F8H2-MAM ($\Delta x = 0\%$) and F8H2-MAM ($\Delta x = 70\%$) samples, respectively. The solid and open symbols represent $\langle\tau_{\text{F-helix}}\rangle$ measured along and perpendicular to, respectively, the stretching direction. The dashed line marks the value of $\langle\tau_{\text{F-helix}}\rangle$ corresponding to a completely disoriented MAM. The solid lines are meant to guide the eye.